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The Preparation and Properties of Aluminium Fluoride

By

T. R. Scott, M.Sc.

(*Division of Industrial Chemistry*)

MELBOURNE, 1947

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SUMMARY

Aluminium fluoride is one of the minor constituents added to the electrolytic cells during the production of metallic aluminium, some thousands of tons being required annually because of the very large output of the metal. No natural deposits of this compound are known and it must therefore be manufactured, not only for the aluminium industry, but also for use in ceramics and metallurgy.

In this bulletin, methods which have been used or proposed for the manufacture of aluminium fluoride are critically reviewed and a choice made of the most suitable method for producing a high-grade material, preferably working in conjunction with a Bayer-plant for the production of aluminium from bauxite.

The selected method utilizes hydrofluoric acid and aluminium hydroxide (or the metal itself) as the sources of fluorine and aluminium respectively. Problems associated with the preparation of solutions of aluminium fluoride from these reagents are discussed and include difficulties arising from corrosion, the use of impure reagents and the metastable nature of the solutions.

Hydrated aluminium fluoride is recovered from the solutions in 80-85 per cent. yield by a process of high-temperature crystallization, in the presence of acid and seed crystals. Although the method is not new, the variables affecting the crystallization are described in considerably greater detail than has previously been attempted. The particular advantages of this stage in the process are the high purity of the hydrated fluoride, even when crystallized from solutions contaminated with various impurities, and its granular nature, which enables filtering and washing to be accomplished with great ease.

Conditions for the dehydration of the hydrated fluoride are also discussed, and, at each stage of the process, suggestions are made for suitable corrosion-resistant equipment.

The aluminium fluoride produced contains less than 0·3 per cent. of water, 0·1 per cent. of silica, and approximately 5 per cent. of alumina. No other impurities are present in significant amounts.

By recycling of mother liquor from the crystallization stage and by preparing solutions in such a way as to leave the minimum quantity of useless residue, approximately 90 per cent. of the fluorine and aluminium introduced in the reagents is converted to anhydrous aluminium fluoride.

The Preparation and Properties of Aluminium Fluoride*

I. INTRODUCTION

During the electrolytic reduction of alumina dissolved in molten cryolite, fluorine is lost from the electrolyte by volatilization of aluminium fluoride and by partial electrolysis of the cryolite itself (23). Further quantities of aluminium fluoride are lost by reaction with certain of the metallic oxide impurities in the alumina and electrodes, forming the corresponding metallic fluorides and alumina. It is therefore customary to add small quantities of aluminium fluoride to the cell at intervals to compensate for these losses, the amount required being 0·3-1·0 per cent. of the primary aluminium output (4). This procedure has the further advantage of minimizing the production of sodium at the cathode (9), and the addition of somewhat larger quantities is said to be beneficial in the electrolysis of alumina containing considerable quantities of alkali (23). In the Hoopes process for the refining of aluminium metal, the electrolyte contains 13-18 per cent. of aluminium fluoride as well as 42-50 per cent. of cryolite. Aluminium fluoride is also used in the preparation of white enamels and fluorine-containing glasses, as a constituent of welding fluxes, and as an anti-reflection coating in complex optical systems.

The rare mineral fluellite ($AlF_3.H_2O$) is the only fluoride of aluminium occurring in the natural state. Manufacture of the compound has therefore been undertaken in most countries producing aluminium, but, although brief accounts have been given of the methods of preparation employed in U.S.A.(4) and Germany (3), no specifications for aluminium fluoride, as used in the aluminium industry, have appeared in the literature. Presumably, the maximum content of impurities should be of the order specified for cryolite (6), viz., 0·3 per cent. silica and 0·06 per cent. Fe_2O_3. According to Callahan (4), commercial aluminium fluoride produced in U.S.A. contains 85 per cent. AlF_3 and less than 5 per cent. water, the balance consisting of silica, alumina, and aluminium sulphate. In the present investigation, the aim has been to produce a material of considerably higher grade (90-95 per cent. AlF_3), substantially free from silica and aluminium sulphate, and uncontaminated by salts produced by corrosion of equipment.

Before proceeding to the experimental part of the present work, it is desirable to review and discuss the methods for the production of aluminium fluoride which have appeared in the literature. A brief review has already been made by Edwards, Frary, and Jeffries (9), but is chiefly concerned with the use of hydrofluoric acid and other fluorides in extracting alumina from its ores; moreover, much useful information has appeared since the date of publication of their work

* Typescript received May 28, 1947.

(1930). Since, in most of the methods to be described, one or other of the hydrates of aluminium fluoride is prepared, the review will be preceded by a brief account of the relevant properties of the hydrates.

II. HYDRATES OF ALUMINIUM FLUORIDE

Although many hydrates of aluminium fluoride have been described, elucidation of their nature has been hampered by the existence of isomeric hydrates having different physical properties and by the slowness with which metastable forms change to the stable forms. A list of the known hydrates and their compositions is given in Table 1.

TABLE 1.—HYDRATES OF ALUMINIUM FLUORIDE

Compound.	Al.	F.	H_2O.
	%	%	%
$AlF_3.9H_2O$	10·96	23·16	65·88
$AlF_3.3·5H_2O$	18·37	38·77	42·86
$AlF_3.3H_2O$	19·57	41·30	39·13
$AlF_3.H_2O$	26·44	55·90	17·66
$AlF_3.0·5H_2O$	29·00	61·31	9·69
AlF_3	32·11	67·89	..

$AlF_3.9H_2O$

This salt is obtained in transparent crystals by cooling concentrated solutions of aluminium fluoride to 0-10°C. It was first prepared by Mazzucchelli (16), who gave the formula as $Al_2F_6.17H_2O$, but later work by Tosterud (33) showed that nine molecules of water were associated with each molecule of the salt. This hydrate is metastable even at 0°C., being much more soluble than the trihydrate at this temperature. The solubility is variously given as 0·86 (37) and 1·2 (16) g. AlF_3 per 100 g. of solution at 0°C., increasing very greatly with temperature. At room temperatures, the crystals are efflorescent and gradually change to a lower hydrate, the exact nature of which is still undecided. In the presence of solutions of aluminium fluoride above 8°C., solid $AlF_3.9H_2O$ is transformed to a soluble form of $AlF_3.3·5H_2O$ (37).

$AlF_3.3·5H_2O$

Yatlov and Pinayevskaya (37) have recently described two forms of this hydrate, distinguished as soluble (β) and insoluble (α). The former is the compound obtained by the well-known method of adding alcohol to a concentrated solution of aluminium fluoride; the latter is obtained by the spontaneous crystallization of solutions at room temperature. Both forms are metastable over the temperature range 0-100°C., since even the so-called insoluble form is nearly twice as soluble as the stable trihydrate. In contact with solutions of aluminium fluoride, these hydrates are transformed to the stable trihydrate, the

change occurring rapidly at high temperatures. At room temperatures, the solid crystals change very slowly, a period of three months being required even for the less stable β-form.

$AlF_3.3H_2O$

Two isomers of this hydrate have been prepared by Ehret and Frere (10), the soluble (α) form being obtained when concentrated (20 per cent.) solutions are prepared at temperatures below 25 C. and cooled in an ice-chest. The insoluble (β) form is made by crystallization at 75-100°C., preferably accompanied (37) by vigorous stirring. This is the stable salt between 0° and 100°C., the solubility being 0·41 g. AlF_3 per 100 g. of solution at 25°C. It is unfortunate that independent workers (10, 37) have adopted conflicting symbols to designate soluble and relatively insoluble hydrates. Yatlov and Pinayevskaya regard the soluble $AlF_3.3H_2O$ as being identical with soluble $AlF_3.3.5H_2O$. They claim to distinguish between the corresponding insoluble forms by differences in refractive index of the crystals and state that a series of solid solutions, characterized by a gradual change in refractive index, exists between these two forms. It is certainly true that the stable trihydrate nearly always contains between 3·0 and 3·5 molecules of water to each molecule of aluminium fluoride, and the excess water is very difficult to remove. Ehret and Frere, however, have demonstrated with certainty that, under equilibrium conditions, the stable salt has the composition $AlF_3.3H_2O$ and they have been unable to detect any differences between the X-ray diffraction pattern of salts varying in composition from $AlF_3.2·86H_2O$ to $AlF_3.3·5H_2O$.

$AlF_3.H_2O$

This hydrate occurs in nature as the mineral fluellite, crystallizing in the orthorhombic system. Mazzucchelli (16) found that material of this composition (Table 1) was formed when clear solutions of aluminium fluoride were evaporated to dryness at 100°C. Microscopic examination of similar material, however, has shown it to be optically isotropic and X-ray diffraction patterns have disclosed no evidence for $AlF_3.H_2O$, though lines characteristic of AlF_3 and $AlF_3.3H_2O$ were present. Yatlov and Zelyanskaya (38) found no evidence for the existence of the monohydrate in their study of the vapour pressure of hydrated aluminium fluoride at different temperatures. It is possible, therefore, that the compound has not yet been prepared in the laboratory.

$AlF_3.0·5H_2O$

Yatlov and Zelyanskaya prepared this salt by slow desiccation of the trihydrate at 120°-130°C., and found the vapour pressure to be 5·5 mm. Hg at 90°C., compared with 424 mm. Hg for the trihydrate at the same temperature. It is perhaps significant in this connection that Tosterud (33) observed a sudden change at 120°-125°C., in the X-ray diffraction patterns of $AlF_3.9H_2O$ which was undergoing progressive dehydration. The water content of his salt at 125°C. was 11·91 per cent. (cf. Table 1). The hemihydrate undergoes partial decomposition in the temperature range 200°-350°C., but a final temperature of 700°-800°C. is required for complete dehydration of bulk samples.

III. REVIEW AND DISCUSSION OF METHODS

Although hydrofluoric acid is the fluorine compound most commonly employed in the preparation of aluminium fluoride, suggestions have also been made for the use of aluminium fluosulphate, fluosilicic acid, and silicon tetrafluoride. An account of the preparation and purification of these reagents has been given elsewhere (6).

1. Methods using Aluminium Fluosulphate

This reagent is obtained by boiling concentrated solutions of aluminium sulphate with finely-ground fluorspar.

$$Al_2(SO_4)_3 + 2CaF_2 \longrightarrow (AlF_2)_2SO_4 + 2CaSO_4$$

On the addition of ammonia (not more than 20 per cent. excess), basic aluminium fluoride is quantitatively precipitated (22).

$$(AlF_2)_2SO_4 + 2NH_4OH \longrightarrow 2AlF_2(OH) + (NH_4)_2SO_4$$

This compound, which may be dehydrated at 500°-600°C., has been suggested (13, 19) as a substitute for aluminium fluoride in the electrolysis of alumina, but there are no indications that such a change has occurred in works practice anywhere. Moreover, the gelatinous precipitate is difficult to wash and filter, somewhat variable in composition, and contaminated with ammonium fluoaluminates (5). The basic fluoride may also be obtained, without the use of ammonia, by autoclaving fluosulphate solutions at 150°-170° for 1·5 hours (15), but the yield does not exceed 70-75 per cent. and the product contains sulphate as an impurity.

The hydroxyfluoride decomposes at 500°-600°C. to a mixture of aluminium oxide and fluoride (5), and the latter salt may be separated by sublimation at 1,100°C.(13), but the method does not appear to have any practical value. A similar criticism applies to the unusual process (18) involving the direct distillation of a fluorspar-kaolin mixture. It has also been suggested (27) that, after heating aluminium fluosulphate to 200°-300°C., the water-soluble aluminium sulphate may be leached away to give a residue of aluminium fluoride; laboratory trials, however, have failed to confirm this claim.

In the ternary system AlF_3—$Al_2(SO_4)_3$—H_2O at 25°C., the solubility of aluminium fluoride never exceeds 6 g./100 g. of solution (10). Solutions prepared by Nikolaev (22), containing 16 per cent. AlF_3, are thus metastable at this temperature, but attempts by the writer to crystallize the aluminium fluoride in excess of 6 per cent. have been unsuccessful, both at room temperatures and at 90°-100°C.

The only practicable method which has been suggested for the recovery of aluminium fluoride from fluosulphate solutions is described in a Russian patent by Kametskii and Kashcheev (14) and makes use of the reaction:—

$$(AlF_2)_2SO_4 + 2HF \longrightarrow 2AlF_3 + H_2SO_4$$

By adding a 5-10 per cent. excess of acid to concentrated solutions, and heating at 50°-100°C. for some hours, yields of 75-85 per cent. are said to be obtained. Nikolaev (22) failed to obtain aluminium fluoride by this method, but calculations made on his reported results indicate that the amount of acid used by him was inadequate.

Although the patent expressly stipulates that fluosulphate solutions must be concentrated by evaporation until the fluorine content is 10-12 per cent., the writer has obtained equally good yields from solutions of half this strength by seeding with crystals of β-$AlF_3.3H_2O$. The method has the important advantage that the sulphuric acid in the mother liquor may be neutralized with aluminium hydroxide and the resulting solutions reacted with fluorspar to re-form aluminium fluosulphate.

Although Russian workers imply that solutions having the composition $(AlF_2)_2SO_4$ are formed when the theoretical quantities of fluorspar and aluminium sulphate are allowed to react, the writer has found that these solutions are hydrolysed by boiling, with precipitation of basic aluminium fluoride. In this way, 10-20 per cent. of the aluminium and fluorine is lost and proportionately greater quantities of hydrofluoric acid must be added before aluminium fluoride can be recovered from solution.

2. Methods using Fluosilicic Acid and Silicon Tetrafluoride

By treating kaolin or aluminium hydroxide (24) with hot fluosilicic acid, or by passing silicon tetrafluoride into a suspension of clay (12), solutions of aluminium fluosilicate may be obtained. When excess hydrofluoric acid is added to these solutions in the cold, aluminium fluoride is said to be precipitated and fluosilicic acid regenerated for further use (35). Alternatively, silica may be precipitated by the addition of excess alumina, leaving aluminium fluoride in solution, whence it may be recovered by methods to be described in the next section.

In practice, however, great difficulty is experienced in separating the solutions from the precipitated silica, and, although the difficulty may be overcome by working with dilute (1-3 per cent.) solutions, methods for the recovery of aluminium fluoride from such solutions are unsatisfactory when compared with those for more concentrated solutions obtained by other reactions.

Another process involves the decomposition of solid aluminium fluosilicate at temperatures around 600°C., the evolved silicon tetrafluoride being combined with hydrofluoric acid to re-form fluosilicic acid (34). According to Sanfourche and Krapivine (28), however, solutions of aluminium fluosilicate are unstable and the products of hydrolysis are exceedingly varied. Moreover, the solid salt undergoes extensive thermal hydrolysis when attempts are made to effect its dissociation into silicon tetrafluoride and aluminium fluoride. It is probable, therefore, that aluminium fluoride produced by such methods would be contaminated with undesirably large amounts of impurities.

3. Methods using Hydrofluoric Acid

By passing gaseous hydrogen fluoride over alumina or aluminium hydroxide at temperatures variously described as up to 200°C.(39) or between 400° and 700°C.(36), anhydrous aluminium fluoride is obtained in one operation. From a study of the kinetics of the method (32), it has been shown that the crust of aluminium fluoride

formed on the particles of alumina retards the reaction in the later stages and it is thus uneconomical to attempt the production of a material containing more than 88-92 per cent. aluminium fluoride. The product is generally contaminated with aluminium sulphate derived from the sulphuric acid mist present in the gas and with all non-volatile impurities originally present in the alumina. The method has the virtue of simplicity, though difficulties are probably experienced in providing suitable corrosion-resistant equipment.

In the majority of methods, solutions of hydrofluoric acid are reacted with various materials containing aluminium, such as aluminium shavings (32), aluminium hydroxide (23), kaolin (26), bauxite (8), felspar (7), &c. With the solutions obtained from impure source materials, silica is precipitated by the addition of excess alumina, and metallic impurities by the passage of hydrogen sulphide. From kaolin and felspar, however, the quantity of precipitated silica obtained is even greater than in the reaction between fluosilicic acid and aluminium hydroxide (see above) and methods employing these materials are consequently impracticable. Solutions of aluminium fluoride obtained from purer source materials are treated for the recovery of aluminium fluoride by one of the following methods.

(i) *Evaporation to Dryness* (11)

This procedure is only practicable when dealing with solutions which are both pure and very concentrated. Even under these circumstances, difficulties may arise owing to the tendency of such solutions to form a gummy mass during evaporation.

(ii) *Precipitation of Ammonium Fluoaluminates*

By adding ammonium fluoride to solutions of aluminium fluoride, a precipitate containing various ammonium fluoaluminates is formed. The solid may be recovered by filtration and decomposed by heating to 700°C.(1), the non-volatile residue consisting of anhydrous aluminium fluoride. A similar product is obtained by dissolving alumina or aluminium hydroxide in excess hydrofluoric acid, and completing the neutralization with ammonia. A related process has been suggested (2) in which solid aluminium hydroxide is heated with solid ammonium bifluoride. In all these methods, the major part of the ammonium fluoride evolved during calcination can be recovered and used again.

(iii) *Low-temperature Crystallization*

Nikolaev and Koltypi (23) have made a detailed study of this technique, using solutions prepared from hydrofluoric acid and aluminium hydroxide. By cooling to 0°C. for three hours, with constant stirring, recoveries were as high as 94 per cent. When the time of crystallization was limited to one hour, yields were considerably less. The solubility of the salts precepitated (presumably a mixture of $AlF_3.9H_2O$ and α-$AlF_3.3H_2O$) increased sharply with temperature, and, at 20°C., recoveries did not exceed 70 per cent.

The concentration of hydrofluoric acid also had important effects upon the results. Using 12 per cent. acid, under what were otherwise optimum conditions, the maximum yield was 68 per cent., owing mainly to the slower rate of crystallization.

Under the same conditions, but with 20 per cent. acid, the maximum yield was 94 per cent. In agreement with Tishchenko and Levina (32), the authors found that results were only satisfactory if a surplus of at least 6, and preferably 10, per cent. acid was used. This ensured that complete solution of the aluminium hydroxide was effected and made possible much higher yields than could be obtained from solutions containing less, or no, free acid.

(iv) *High-temperature Crystallization*

Various techniques have been described for the precipitation of aluminium fluoride from *heated* solutions, and include suggestions that crystallization may be initiated by the presence of finely-divided inert material (20) and that the precipitate acquires a granular form in the presence of excess hydrofluoric acid (17). When crystallization has been initiated with β-$AlF_3.3H_2O$, the aluminium fluoride obtained is remarkably free from impurities such as silica, in contrast to the material produced by low temperature crystallization, which contains 0·5-0·7 per cent. silica (23). From clear and undisturbed solutions, the so-called monohydrate described by Mazzucchelli (16) may form, but the stable trihydrate is always formed in acid solutions and in the presence of seed crystals. Yields as high as 80 per cent. may be obtained under optimum conditions (q.v.) even from solutions much more dilute than those required for satisfactory low-temperature crystallizations.

Reports on the production of aluminium compounds in Germany(3) state that aluminium fluoride is prepared on the industrial scale by reacting aluminium hydroxide with 40 per cent. hydrofluoric acid. The hot solution is run into crystallizing vats where it sets to a solid mass, which is chipped out, crushed, and calcined. This relatively crude method has the disadvantage that all impurities are included in the product and some difficulty may be experienced in preventing spontaneous crystallization of the exceedingly concentrated solutions in the reaction vessels.

IV. EXPERIMENTAL

While the primary purpose of the present investigation has been to produce a high grade of aluminium fluoride, as stipulated on page 7, an additional aim has been to use a method of preparation which can conveniently be operated in conjunction with a Bayer-process aluminium plant, using materials available therefrom. This implies the use of hydrofluoric acid (required also for the production of synthetic cryolite) and aluminium hydroxide or metal, though aluminium sulphate could be readily produced if required for the production of fluosulphate solutions. The latter still require the addition of large amounts of hydrofluoric acid to allow recovery of aluminium fluoride, and there appears to be no advantage in preparing two separate fluorine compounds from fluorspar, when a satisfactory method exists which requires hydrofluoric acid alone. The reaction between hydrofluoric acid and aluminium hydroxide (or metal) has therefore been selected as the most suitable for the production of aluminium fluoride.

Of the four methods described in the previous section for the recovery of aluminium fluoride from solution, evaporation to dryness is uneconomical, and low temperature crystallization requires very concentrated solutions and produces material contaminated with silica and other impurities. Precipitation of ammonium fluoaluminate also suffers from the disadvantage of co-precipitation of impurities, while the subsequent recycling of ammonium fluoride may introduce considerable difficulties. High-temperature crystallization avoids most of these difficulties and is regarded as all the more worthy of investigation because it has been comparatively neglected in the past. The method has been used on a commercial scale in U.S.A., but, from the description given (4), it seems that the numerous variables have not been wholly appreciated or brought under control.

The preferred process can be conveniently divided into three stages, viz.:—

1. Preparation of solutions.
2. Crystallization of aluminium fluoride trihydrate.
3. Dehydration of aluminium fluoride trihydrate.

The disposal of mother liquor from the crystallization stage will be discussed under the first of these headings. Since the requirements for corrosion-resistant equipment vary considerably from stage to stage, corrosion problems will be dealt with as they arise.

1. Preparation of Solutions

Although the solution of aluminium or pure aluminium hydroxide in hydrofluoric acid is fundamentally a simple process, difficulties have arisen in the present investigation owing to—

(i) the metastable nature of aluminium fluoride solutions,
(ii) the use of relatively impure commercial grades of reagents,
(iii) the need for recirculation of mother liquors and solid residues,
(iv) the corrosive nature of the solutions employed.

These difficulties will be discussed in the above order. It must be stressed that the methods proposed in the following sections have been developed in the laboratory and may therefore require modification when applied on an industrial scale.

(i) *Metastable Nature of Solutions*

Clear solutions of aluminium fluoride, containing up to 10 per cent. AlF_3, may be kept at room temperatures for some days without deposition of the trihydrate, but simple stimuli, such as stirring, addition of seed crystals, or increase in temperature, are sufficient to initiate crystallization at an appreciable rate within a few hours. The process is nevertheless comparatively slow and yields are not high unless all three stimuli are applied simultaneously (q.v.).

With more concentrated solutions, prepared from 10-40 per cent. hydrofluoric acid (3, 23, 32), the rate and extent of deposition of trihydrate are less predictable and solutions may even become turbid before the neutralization is completed. Because of the difficulty of controlling the behaviour of such solutions, the present work has been confined to the more dilute solutions prepared from 6-7 per cent.

acid. Even so, care must be exercised in the preparation of solutions, since the exothermic nature of the reaction and the presence of suitable seed material (when aluminium hydroxide is the reagent) favour the comparatively rapid deposition of trihydrate. Moreover, the final stages of neutralization are only slowly completed and the acid nature of the solution during this period further assists the process of crystallization. The aluminium fluoride deposited in this way is contaminated not only with unreacted aluminium hydroxide, but also with insoluble impurities present in the reagents and thus fails to comply with the purity requirements stipulated on page 7. In some processes for the preparation of aluminium fluoride, it appears that this contamination is tolerated (3, 4, 23) and the two processes of solution and crystallization are allowed to overlap.

In the present work, contamination is largely avoided by reducing the time for which solutions are left in contact with excess reagent and maintaining the concentration of solutions within the range of 8-11 per cent. AlF_3. In the preparation of more concentrated solutions, spontaneous crystallization is difficult to control and the temperature rise during the exothermic reaction is excessive. Mulert (21) has found the heat of solution of aluminium hydroxide in 20 per cent. hydrofluoric acid to be 70 cal./mole. This is sufficient to boil the resultant solution, whereas neutralization of 6-7 per cent. acid results in a temperature rise of no more than 30-40 deg. C. With a 10-20 per cent. excess of aluminium hydroxide, reaction is substantially complete (i.e., $pH > 2 \cdot 0$) within 3-4 hours, and the clear solution may then be decanted from the residual solids, which contain only small amounts of crystalline aluminium fluoride. Should these solutions be left in contact with the residue overnight, however, up to 30 per cent. of the dissolved aluminium fluoride may be deposited.

(ii) *Use of Impure Reagents*

The chief impurity found in hydrofluoric acid is fluosilicic acid, which reacts with aluminium hydroxide to produce aluminium fluoride and colloidal silica. The quantities generally present (approximately 5 per cent. in commercial 40 per cent. hydrofluoric acid) are not sufficient to cause contamination of the recovered aluminium fluoride.

Commercial grades of aluminium hydroxide frequently contain silica (up to 1 per cent.) and sodium carbonate. The silica is dissolved when hydrofluoric acid is added and forms fluosilicic acid. Claims have been made that silica is precipitated by the addition of excess aluminium hydroxide (7, 11), but such precipitation is by no means quantitative even in highly siliceous solutions. Experiments have shown that up to 1·5 per cent. of silica may remain in colloidal solution in substantially neutral solutions containing 8-10 per cent. AlF_3 and this silica is not deposited when solutions are maintained at 90°-100°C. for several hours. It is thus possible to crystallize pure β-$AlF_3.3H_2O$ from the solutions despite the presence of silica.

Sodium carbonate, however, reacts with aluminium fluoride to produce chiolite, with resultant losses of aluminium and fluorine. With a sample containing 6·3 per cent. Na_2O, 15 per cent. of the fluorine was lost in this fashion. It is thus desirable to leach impure aluminium hydroxide with sufficient sulphuric or hydrochloric acid

to remove the greater part of the sodium, 0·25 per cent. of Na_2O being regarded as the upper limit for this contaminant. This procedure has been successfully used in the laboratory, little alumina being dissolved and no serious difficulty being experienced in filtering the leached material.

Experiments have been conducted by the writer with bauxite as the source of aluminium, but considerable amounts of acid are wasted in dissolving oxides of iron, titanium, &c., present in this material. It is nevertheless possible to recover aluminium fluoride containing less than 0·1 per cent. Fe_2O_3 from the resulting solutions, using the method of high-temperature crystallization. Evaporation must be restricted during the crystallization, however, to avoid a marked increase in contamination due to increase in concentration of the soluble impurities. This difficulty also arises when attempts are made to recycle the mother liquor from the crystallization, and the advantage of using bauxite as a cheap source-material is thus nullified by the losses of fluorine incurred when the heavily contaminated mother liquors are necessarily discarded.

When aluminium metal (scrap) is used to prepare solutions, minor alloying constituents such as magnesium form insoluble precipitates, while impurities such as iron, copper, and silicon remain in solution and do not interfere with the subsequent crystallization of aluminium fluoride. The need for discarding mother liquors depends entirely on the composition of the metal used, but it is unlikely that the proportion of impurities will be as great as in bauxite and some recirculation of mother liquors will generally be possible.

(iii) *Recirculation of Mother Liquors and Residues*

When an excess of aluminium hydroxide has been used for preparing solutions, as described on page 15, the slurry left after decanting the solution cannot be discarded, since it contains unreacted hydroxide and portion of the aluminium fluoride solution. Treatment of the slurry with excess of fresh hydrofluoric acid (6-7 per cent.) leaves a considerable proportion of the solid fraction undissolved, presumably because of a protective coating of chiolite or aluminium fluoride on the aluminium hydroxide. Complete solution of all but the chiolite can only be effected by heating the slurry with concentrated (25-40 per cent.) hydrofluoric acid, which dissolves the deposit of aluminium fluoride on the particles of hydroxide. The solution so obtained may then be diluted to the usual strength (6-7 per cent. acid) for re-use.

This procedure is not entirely satisfactory, since the hot concentrated acid is highly corrosive and deposition of aluminium fluoride may occur. As an alternative, the relatively large quantity of unreacted hydroxide may be avoided by adding only the theoretical quantity of aluminium hydroxide to 6-7 per cent. acid. Under these circumstances, neutralization of the acid is only 85-90 per cent. complete, but the amount of undissolved material is smaller. The acid solutions of aluminium fluoride may be taken directly to the crystallization stage or the neutralization may first be completed by adding aluminium metal in sufficient quantity. The latter process is preferred since it permits of better control of acidity during the crystallization stage. The small quantity of undissolved material remaining after the solutions have been decanted can be partially

brought into solution with the next lot of 6-7 per cent. acid and the residue accumulated after several such cycles can be discarded without incurring serious losses.

Further tests on the aluminium hydroxide used in these experiments (predominantly bayerite with 0·2 per cent. Na_2O) disclosed that it was not completely soluble even in a 10 per cent. excess of hot or cold 15 per cent. acid, though Nikolaev and Koltypi (23) claimed complete solution under these conditions.

The mother liquor remaining after the high temperature crystallization of β-$AlF_3.3H_2O$ (q.v.) retains about 20 per cent. of the original aluminium fluoride, and is therefore used in the next cycle of operations for diluting 40 per cent. acid. Evaporation during the crystallization stage permits complete use of mother liquor and washings in this way. On a laboratory scale, 50 per cent. reduction in volume is conveniently achieved in the time required to obtain the maximum yield of aluminium fluoride crystals. Further study of this factor will be necessary if the process be adapted to large-scale operations.

Recirculation of mother liquors leads to an increase in the concentration of impurities such as silica and, after 4 or 5 cycles, it is preferable to discard the mother liquor to avoid undue contamination of the next batch of aluminium fluoride. Nevertheless, the total operating losses caused by discarding accumulated residues and contaminated mother liquors should not exceed 10 per cent. of the fluorine used.

(iv) *Corrosion*

Nikolaev and Koltypi (23) prepared solutions of aluminium fluoride in lead-lined reactors, but the writer has shown (29) that such material is quite unsuitable. The coating of lead fluoride, which normally protects lead vessels from corrosion in the presence of hydrofluoric acid, is freely soluble in solutions of aluminium fluoride. As a result the metal undergoes severe corrosion and the aluminium fluoride eventually recovered from solution is contaminated with lead fluoride. Monel and copper are more resistant than lead, but undergo slow corrosion, particularly at the liquid level, at elevated temperatures. It is best to use equipment lined with rubber or made from impervious carbon. The maximum temperature occurring during solution of the aluminium hydroxide is not in excess of that permissible for rubber-lined apparatus.

2. Crystallization of Aluminium Fluoride Trihydrate

Under optimum conditions, the process to be described yields crystalline aluminium fluoride which is easy to filter and wash, and contains as the only significant impurity no more than 0·1 per cent. of silica. The method has been referred to as " high-temperature " crystallization to distinguish it from the method used by Nikolaev and Koltypi (q.v.), but high temperatures, though desirable for other reasons, are actually not essential for the crystallization of β-$AlF_3.3H_2O$. In the presence of acid and seed crystals, with continual stirring, reasonable yields are obtained even at room temperatures, over a period of 2-3 days. At temperatures approaching 100° C., the same

hydrate is produced simply by the vigorous stirring of concentrated solutions (10, 37) without the addition of acid or seed. The product in this latter instance contains very minute crystals which cause great difficulty in filtering and washing and tend to carry down appreciable quantities of impurities. It is only by the use of acid and seed crystals that rapid deposition of material having desirable physical properties can be achieved. Hydrofluoric acid is most suitable for acidifying the solutions, since other acids introduce foreign anions which complicate the recycling of mother liquors.

Optimum conditions for the process have been established by considering the following factors:—

(i) Quantity of acid added to neutral solutions.
(ii) Quantity and nature of seed used.
(iii) Temperature of solutions.
(iv) Time allowed for heating and cooling of solutions.
(v) Concentration of solutions.
(vi) Nature and extent of stirring.
(vii) Reduction in volume by evaporation.

The crystallization was carried out in monel beakers, using silver-plated stirrers. The trihydrate was recovered by filtration, washed with small quantities of water and alcohol and dried at 100°C. As noted by Ehret and Frere (10), the product usually contained an excess of water of crystallization and yields were calculated on the assumption that material had the composition $AlF_3.3{\cdot}5H_2O$. X-ray diffraction patterns of the compound were nevertheless identical with those for $AlF_3.3H_2O$.

Since most of the above factors are interdependent, preliminary experiments were required to determine the most important variables and to eliminate from further consideration those requiring little control. As seed material, crystalline trihydrate dried at 100°C. was used exclusively. Solutions were cooled from 95° to 25°C. over a fixed period of 90 minutes before filtering, no significant increase in yield being observed by prolonging the period to 24 hours. Continuous stirring and evaporation of solutions during crystallization both led to higher yields, but the study of other more important variables was greatly simplified by conducting the crystallization in closed vessels and limiting the stirring to that needed to keep fine seed crystals in suspension (i.e., stirring at 10-minute intervals). The remaining variables were then varied one at a time with the following results:—

(i) *Quantity of Hydrofluoric Acid*

Experiments were conducted at 95 ± 2°C. with 100 ml. of solution containing 8·9 g. AlF_3 using 3 g. of seed and adding varying amounts of acid. With less than 0·5 per cent. hydrogen fluoride crystallization occurs but filtration of the product is almost impossible. With greater amounts of acid, the material is coarsely crystalline and easily filtered, but relatively large (3 per cent.) quantities of acid cause the yield to decrease by 7-8 per cent. as might be expected from the known solubility of aluminium fluoride in hydrofluoric acid. Best yields were obtained with 0·5-1·0 per cent. hydrogen fluoride and all succeeding crystallizations have therefore been done with

0·75 per cent. in solutions of the above strength. The same proportion of acid to aluminium fluoride has been preserved in dealing with solutions of different concentrations and represents a 14 per cent. excess of acid.

(ii) *Quantity of Seed*

In solutions containing 8·9 g. AlF_3 per 100 ml., the quantity of seed was varied from 0·5-6·0 g. per 100 ml. Maximum yields at 95 ± 2°C. were obtained with 4-5 g. of seed, but were only 4 per cent. greater than the average yield with small amounts of seed. In the latter instance, adherent crystals tend to form on the sides of the vessel and on the stirrer, but this minor difficulty would be largely overcome by continuous stirring. On an industrial scale, the deciding factors might well be the quantity of liquor which could be decanted from the crystals and the amount of wash water required to remove the bulk of the mother liquor from the crystals. Under these circumstances, use of the minimum bulk of seed would possibly be preferred.

(iii) *Temperature*

The variation of yield with temperature is shown in Table 2. The solutions employed contained 8·4 g. AlF_3 per 100 ml. and were maintained at the stipulated temperature for 135 minutes. The same quantities of seed and acid were used throughout, but yields were slightly low because the optimum quantities were not known when the work was done.

TABLE 2.—VARIATION IN YIELD OF β-$AlF_3.3H_2O$ WITH TEMPERATURE.

Temperature (± 1°C.).	Yield.
°C.	%
25	7·0
41	23·0
50	29·2
65	52·2
79	58·5
90	59·2
97	60·0

By prolonging the treatment at lower temperatures, increased yields could of course be obtained.

In subsequent experiments, samples were heated in a water bath at 95 ± 2°C., the error introduced by such variation in temperature being evidently unimportant.

(iv) *Time of Stirring*

The time of stirring required to achieve the maximum yield is dependent on temperature and concentration of solutions. For practical purposes, however, it was only important to know the time required for concentrated solutions treated at the optimum temperature (90-100°C.). In solutions containing 7·9 g. AlF_3 per 100 ml., no significant increase in yield occurred after heating for 135 minutes with occasional stirring, and deposition is more rapid with more concentrated solutions. Weaker solutions would not be used on an industrial scale, but it is interesting to note that the yield from 5·5 per cent. solutions increases from 40 per cent. in 135 minutes to

61 per cent. in 540 minutes. At room temperatures, however, two days of continuous stirring are required to obtain a 60 per cent. yield from 8 per cent. solutions.

(v) *Concentration of Solutions*

The effect of this variable is shown in Fig. 1. The results were obtained at 95 ± 2°C., using the above-mentioned quantities of seed and acid. Solutions were all heated for 135 minutes, which was sufficient to produce the maximum yield in each instance (with the possible exception of the weakest solution).

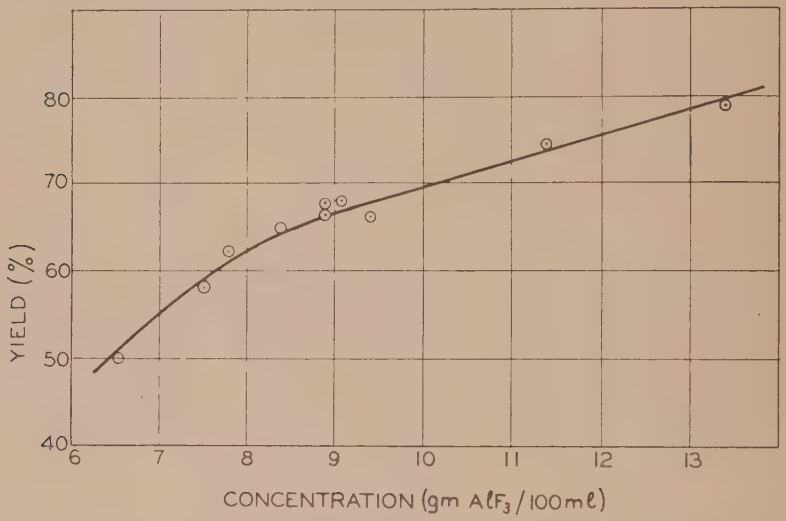

FIG. 1.—Variation of yield of aluminium fluoride with concentration of solutions.

Despite the higher yields obtained with very concentrated solutions, the problems associated with their preparation (page 14) are such that preference is given to the range 8-10 per cent. aluminium fluoride. At these concentrations, approximately 65 per cent. of the aluminium fluoride is obtained in crystalline form in two hours at 95°C. Although yields were based on the assumption that the composition of the material was $AlF_3.3 \cdot 5H_2O$, analyses have shown that the average composition is closer to $AlF_3.3 \cdot 2H_2O$, and all reported yields are therefore low by 3-4 per cent. In addition, it will be necessary in practice to allow free evaporation of the solutions during crystallization (page 17), and tests have shown that this procedure, combined with constant stirring, gives yields of 80-85 per cent. when 8-10 per cent. solutions are evaporated to half their bulk. Crystallization on the sides of the vessel is not overcome by the stirring under these circumstances, but the difficulty may be overcome by heating only half of the solution initially and feeding the remainder dropwise into the vessel at a rate just sufficient to balance evaporation losses. In this manner, the total volume of solution is diminished by 50 per cent., with the volume in the vessel remaining constant throughout.

Although maximum yields are obtained within a few hours, equilibrium conditions are not established, since the concentration of aluminium fluoride in the mother liquors is still much greater than

the value for the solubility of the stable trihydrate at 100°C., given by Yatlov and Pinayevskaya (37). No economic advantage would be gained, however, by prolonging the crystallization period for days in an effort to recover an additional 10 per cent. or so of aluminium fluoride.

Hot acid solutions of aluminium fluoride are very corrosive, silver and platinum being among the very few metals which resist attack. Monel and copper are corroded appreciably in the presence of air, though the soluble copper and nickel fluorides cause no detectable contamination of the crystallized aluminium fluoride. (For filtration of the *cooled* solutions, however, equipment made from monel or Dow metal is reasonably satisfactory.) Impervious carbon or graphite is probably the most suitable material for the crystallization stage, but care must be taken to keep interior surfaces smooth enough to prevent adherence of crystals and subsequent growth of a hard impervious scale of aluminium fluoride.

3. Dehydration of Aluminium Fluoride Trihydrate

The greater part of the water in aluminium fluoride trihydrate can be removed at relatively low temperatures. Yatlov and Zelyanskaya (38) reduced the water content to 9·5 per cent. at 120°-130°C. while Tosterud (33) obtained a figure of 11·9 per cent. after 170 hours at 125°C. The remaining water is more difficult to remove, and commercial grades of aluminium fluoride usually contain appreciable amounts. According to Callahan (4), calcination at 650°C. for 45 minutes yields a product with less than 5 per cent. water, while Nikolaev and Koltypi (23) found that drying for 48 hours at 350°-400°C. reduced the water content to 2·0-2·5 per cent. For the production of substantially anhydrous material ($< 0{\cdot}3$ per cent. water), the choice lies between prolonged heating at moderate temperatures (circa 500°C.) or brief heating in a matter of minutes at 700°-800°C. Higher temperatures cause appreciable volatilization of aluminium fluoride and are therefore avoided.

It is preferable to remove the major part of the water by drying for 12-24 hours in the range 150°-200°C. This enables the more easily removed water to be evolved quietly and avoids the spurting which occurs if the trihydrate is placed directly into a furnace at 500°-750°C. The remaining water may then be driven off by ignition at 700°-800°C. for 30 minutes.

Fluorine is invariably lost by thermal hydrolysis. This phenomenon is appreciable at 500°C. but is most marked at higher temperatures. The results given in Table 3 show the effect of ignition at 750°C. on material previously treated at 500°C. for one hour.

TABLE 3.—COMPOSITION OF IGNITED ALUMINIUM FLUORIDE

Time of Heating at 750°C.	AlF_3.	Al_2O_3.	Water.
Mins.	%	%	%
Nil	93·3	2·3	4·4
5	96·1	2·8	1·1
15	95·6	4·1	0·3
30	94·3	5·6	0·1
60	91·6	8·3	<0·1
240	85·5	14·4	<0·1

The loss of fluorine shown by the last two samples was caused by reaction of the aluminium fluoride with moisture of the air inside the furnace. The samples consisted of 10 g. of material and were heated in platinum crucibles.

It is possible that hydrates other than β-$AlF_3.3H_2O$ might be dehydrated completely at lower temperatures or be less subject to thermal hydrolysis during evolution of the water. This possibility has not been examined further since the other hydrates cannot be produced in as pure a form.

Several authors (3, 23) describe the use of iron vessels or iron furnace-linings during the calcination stage, but the release of hydrogen fluoride during the process causes severe corrosion and leads to contamination of the product with iron compounds. A much more suitable material is refractory alumina which can be used as a lining both for the kiln or furnace and the vessels containing the aluminium fluoride.

V ANALYTICAL METHODS

Methods for the determination of aluminium, fluorine, sodium, and water in synthetic cryolite have been discussed elsewhere (6), as has a rapid method for determining small quantities of silica in fluorides (30). These methods are equally satisfactory for the analysis of aluminium hydroxide and hydrated aluminium fluoride. It should be noted, however, that recovery of fluorine from the latter compound by the Willard-Winter distillation is often incomplete unless 300-350 ml. of distillate are collected.

Analysis of the ignited fluoride is more difficult, particularly with respect to the determination of fluorine, since the material is only slowly attacked by hot concentrated sulphuric acid. The standard method depends on fusion with alkali carbonates and silica to decompose the sample, followed by neutralization and precipitation of lead chloro-fluoride (31). This procedure is somewhat tedious and tends to give low results in the presence of aluminium; preference has therefore been given in the present investigation to a new method, which is more convenient for routine analyses and has the advantage of incorporating the Willard-Winter distillation in the final stages.

A known weight of aluminium fluoride (approximately 1 g.) is mixed with three times its weight of anhydrous sodium sulphate in a smooth mortar and the mixture placed in a platinum crucible. A smaller amount of sodium sulphate is used to "rinse out" the mortar and is also placed in the crucible. The mixture is heated for 2-3 minutes in a small flame at dull red heat (550°-600°C.) until a clear melt is formed. The cooled melt is weighed, detached from the crucible, and ground in a mortar. A suitable aliquot of the resulting powder is distilled with sand and sulphuric acid by the usual Willard-Winter method and the fluorine content of the distillate determined by titration with thorium nitrate. The entire determination can be completed within three hours.

Aluminium may be conveniently determined on another aliquot of the melt by the usual methods.

The nature of the reaction in the melt is not fully understood, but the matter is under investigation. It is known, however, that sodium sulphate must be present in the molar ratio $Na_2SO_4 : AlF_3$ before

all the fluorine can be distilled, but such melts are glassy and very difficult to crush. With larger quantities of sodium sulphate ($2Na_2SO_4 : AlF_3$), the melts are easily detached from the crucible and can be ground without difficulty. Prolonged heating or the use of excessive temperatures cause loss of fluorine from the melt, but, by using the procedure described above, this loss does not exceed 1·5 per cent. when dealing with anhydrous aluminium fluoride. With the trihydrate, fluorine is also lost by thermal hydrolysis in the early stages of the fusion, and 3-4 per cent. of the total fluorine may escape. The method has nevertheless proved extremely useful for routine anlyses and comparison of samples (as in Table 3 where a correction has been applied for the known losses).

It should be added that a clear melt cannot be obtained with samples containing considerable amounts of alumina, and, in such instances, fusion should not be prolonged beyond the usual three minutes.

VI. CONCLUSIONS

From a survey of known methods of preparation, it has been decided that the reaction between hydrofluoric acid (of commercial grade) and aluminium metal or hydroxide is most suitable for the production of high-grade aluminium fluoride for use in the electrolytic reduction of alumina. These reagents have also been chosen with a view to preparing the material in association with a plant using the Bayer process.

Solutions are prepared in rubber-lined vessels from 6-7 per cent. acid and the theoretical quantity of aluminium hydroxide, neutralization being completed, if desired, with aluminium metal. The use of an excess of aluminium hydroxide to effect neutralization leaves a residue which is not easily soluble in the acid. Crystallization of the solutions is performed at 90°-100°C., in the presence of seed crystals and a 14 per cent. excess of acid. The rate of crystallization is increased by stirring and yields are augmented by allowing solutions to evaporate to half their volume during this stage. The yield of β-$AlF_3.3H_2O$ obtained within two hours is 80-85 per cent., and no important increases occur with a longer period of heating. The crystalline hydrate is filtered and washed, and dehydrated by ignition in two stages, a preliminary stage at 150°-200°C. and a final treatment at 750°C. Mother liquor and washings are combined with 40 per cent. hydrofluoric acid to provide a 6-7 per cent. acid for preparation of further solutions. The crystallization is best undertaken in vessels of graphite or impervious carbon, while alundum is the most suitable material for use in furnace-linings and containing vessels during the dehydration.

The anhydrous aluminium fluoride contains no more than 0·1 per cent. of silica, and considerably smaller amounts of all other impurities. Aluminium oxide is present to the extent of 5 per cent., owing to losses of fluorine during dehydration.

VII. REFERENCES

1. Brit. Aluminium Co. Ltd.—Brit. Pat. 423,601, Feb. 5., 1935 (*Chem. Abs.* 29: 4530 (1935)).
2. Brit. Aluminium Co. Ltd.—Brit. Pat. 425,908, Mar. 20, 1935 (*Chem. Abs.* 29: 6374 (1935)).
3. Brit. Intell. Objectives Sub-Comm.—Final Rept. 764, Item 22. (London: H.M. Stationery Office, 1945.)
4. Callahan, J.—*Chem. Met. Eng.* 52: 94 (1945).
5. Cowley, J. M., and Scott, T. R.—*J. Amer. Chem. Soc.* 69: (in press).
6. Dixon, P., and Scott, T. R.—Coun. Sci. Ind. Res. (Aust.), Bull. 214 (1947).
7. Doremus, C. A.—U.S. Pat. 1,237,488, Aug. 21, 1917 (*Chem. Abs.* 11: 3102 (1917)).
8. Doremus, C. A.—U.S. Pat. 1,391,172, Sept. 20, 1922 (*Chem. Abs.* 16: 318 (1922)).
9. Edwards, J. D., Frary, F. C., and Jeffries, Z.—"The Aluminium Industry." (New York: McGraw-Hill Book Co. Inc., 1930.)
10. Ehret, W. F., and Frere, F. J.—*J. Amer. Chem. Soc.* 67: 64 (1945).
11. I.G. Farbenind. A.-G.—Ger. Pat. 529,602, Jan. 4, 1929 (*Chem. Abs.* 25: 5255 (1931)).
12. I.G. Farbenind. A.-G.—Ger. Pat. 532,859, Apr. 26, 1927 (*Chem. Abs.* 26: 567 (1932)).
13. Ivanov, N. A., Morozov, G. S., and Labutin, G. V.—Russ. Pat. 51,940, Oct. 31, 1937.
14. Kametskii, S. P., and Kashcheev, N. F.—Russ. Pat. 43,417, June 30, 1935.
15. Kashcheev, N. F., and Lazarev, N. V.—Russ. Pat. 46,256, Mar. 31, 1936.
16. Mazzucchelli, A.—*Atti Accad. Lincei* (5) 16: 775 (1907).
17. Milligan, L. H.—U.S. Pat. 1,403,183, Jan. 10, 1922 (*Chem. Abs.* 16: 994 (1922)).
18. Morozov, G. S., and Ivanov, N. A.—Russ. Pat. 52,597, Feb. 28, 1938 (*Chem. Abs.* 34: 5605 (1940)).
19. Morozov, G. S., and Ivanov, N. A.—Russ. Pat. 53,812, Sept. 30, 1938.
20. Morrow, J. E.—U.S. Pat. 1,797,994, Mar. 24, 1931 (*Chem. Abs.* 25: 2819 (1931)).
21. Mulert, O.—*Z. Anorg. Chem.* 75: 198 (1912).
22. Nikolaev, N. S.—*J. Chem. Ind. U.S.S.R.* 14: 1087 (1937).
23. Nikolaev, N. S., and Koltypi, S. G.—Ibid. 11: 53 (1934).
24. Pip, W.—Fr. Pat. 691,419, Mar. 7, 1930 (*Chem. Abs.* 25: 1340 (1931)).
25. Roholm, K.—"Fluorine Intoxication." (London: H. K. Lewis and Co. Ltd., 1937.)
26. Rutgerswerke A.-G.—Ger. Pat. 492,412, Apr. 22, 1926 (*Chem. Abs.* 24: 2842 (1930)).
27. Rutgerswerke A.-G. and Kahl, L.—Fr. Pat. 850,608, Dec. 21, 1939 (*Chem. Abs.* 36: 2095 (1942)).
28. Sanfourche, A. A., and Krapivine, A.—*C.R. Acad. Sci. Paris* 208: 2080 (1939).
29. Scott, T. R.—*J. Coun. Sci. Ind. Res.* (Aust.) 20: 114 (1947).
30. Scott, T. R.—Ibid. 19: 103 (1946).
31. Specht, Fr., and Hornig, A.—*Z. Anorg. Chem.* 125: 161 (1943).
32. Tishchenko, V. E., and Levina, T. A.—*Trans. State Inst. Appl. Chem. U.S.S.R.* No. 16, p. 101 (1932). (*Chem. Abs.* 29: 301 (1935).)
33. Tosterud, M.—*J. Amer. Chem. Soc.* 48: 2 (1926).
34. Wilkinson, J., and Son Ltd., and Saurin, C. J.—Brit. Pat. 421,139, Dec. 14, 1934 (*Chem. Abs.* 29: 3789 (1935)).
35. Wilkinson, J., and Son. Ltd., and Saurin, C. J.—Brit. Pat. 422,080, Jan. 4, 1935 (*Chem. Abs.* 29: 4530 (1935)).
36. Yatlov, V. S., Kovalenko, M. M., and Vinogradova, Z. P.—*J. Appl. Chem. U.S.S.R.* 7: 39 (1934). (*Chem. Abs.* 28: 4969 (1934).)
37. Yatlov, V. S., and Pinayevskaya, E. N.—*J. Gen. Chem. U.S.S.R.* 16: 27 (1946).
38. Yatlov, V. S, and Zelyanskaya, A. I.—Ibid. 7: 1787 (1937).
39. Zimmermann, M.—U.S. Pat. 1,851,475, Mar. 29, 1932 (*Chem. Abs.* 26: 3078 (1932)).

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